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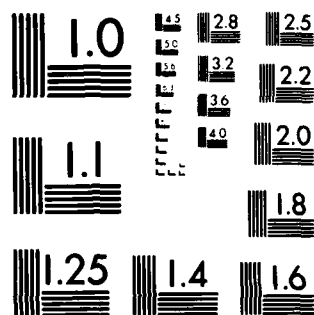
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A TWO PHOTOELECTRODE SOLID-STATE PHOTOELECTROCHEMICAL CELL

By

Anthony F. Sammells and Sharon K. Schmidt

Accepted for Publication
in
Journal of the Electrochemical Society

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The solid-state photoelectrochemical cell p-InP/C ₆₀ H ₂₈ N ₄ Fe ⁺³ Porphine, Nafion 117/Nafion 117/(bpy) ₃ Ru ²⁺ , Nafion 117/n-CdS was prepared and given photopotentials in excess of 1100mV and appears to be a novel approach for not only specialized storage devices but also in specific detector applications.			

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KEY WORDS: Nafion, Indium Phosphide, Cadmium Sulfide, Solid-State Photoelectrochemical Cell



A TWO PHOTOELECTRODE SOLID-STATE PHOTOELECTROCHEMICAL CELL

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The use of solid-electrolyte based photoelectrochemical (PEC) cells provides a unique approach for the PEC conversion and storage of selected redox species incorporated within the proximity of the semiconductor/solid electrolyte interface. For such interfaces, however, the efficient recombination of photogenerated carriers appears to be greatest when both polycrystalline semiconductor and solid electrolyte materials are present at the junction. As a consequence, PEC cells fabricated to contain such interfaces, frequently possess little or no effective photoactivity. To minimize such high population of surface states, single crystal photoelectrodes in contact with solid polymer based electrolytes have been used. We have previously reported on the two photoelectrode cell $p\text{-InP}/\text{PEO}\cdot\text{NaSCN}, \text{Na}_2\text{S}, \text{S}/n\text{-CdS}$ where the sodium ion conducting solid polymer electrolyte (SPE) poly(ethylene oxide) PEO was used.¹ Upon illumination this cell gave photopotentials up to 540mV, however current densities of less than $1 \mu\text{A}/\text{cm}^2$ could only be achieved even under both biased and illuminated conditions. This was in part a consequence of the high resistivity of the SPE material used. PEO had earlier been used in the solid-state PEC cell $n\text{-Si}/\text{PEO}, \text{KI}, \text{I}_2/\text{SnO}_2$ glass, where the $n\text{-Si}$ photoanode was initially coated with platinum and subsequently protected from photoanodic corrosion effects by a sequential layer of platinum and polypyrrole.² For PEO based PEC cells, small interelectrode spacings are desirable for not only minimizing cell IR losses but also for improving light transmission to the solid-

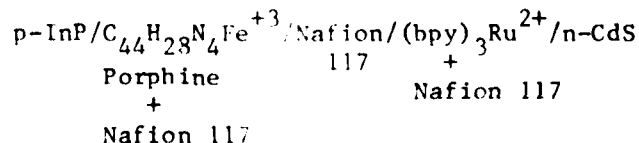
state junction of interest. Achieving small well defined interelectrode spacings can, however, often be logistically somewhat difficult and can frequently lead to cell shorting.

If we wish to introduce some Faradaic storage capacity into a solid-state PEC cell, it will be necessary to provide for effective separation of the oxidant and reductant species which reside close to the appropriate photoelectrode. While this in principle could be achieved using PEO, the preparation of an interelectrode spacing with clearly defined oxidant, separator and reductant regions can be expected to provide a formidable task. This problem has been addressed here by the use of the perfluorinated cation exchange membrane, Nafion,³ as the SPE in a solid-state PEC cell containing potential storage capacity. The PEC activity of semiconductors incorporated onto Nafion in contact with aqueous solutions has been previously reported on, directed towards the photoelectrolysis of water.⁴

As is well known, this material has found extensive application in a variety of electrochemical cells. In addition, redox species such as $(bpy)_3Ru^{2+}$ have been shown to be irreversibly coordinated into Nafion's polymeric matrix where they have exhibited electrochemical reversibility.⁵⁻⁷

Here it appears that the mobile conducting cations are exchanged by the introduced redox species. When such redox containing polymers are attached to an electrode, redox electrochemistry can take place via an electron self-exchange reaction involving the introduced redox species.⁸⁻¹⁰ This SPE material can consist of essentially two phases¹¹ which contain respectively a bulk polymer and a lower density ionic cluster phase. It is in the lower density phase that introduced redox complexes appear to reside. In addition, the higher oxidation states of such complexes appear to be less strongly held than do their lower oxidation states.¹²

We wish to report on the cell



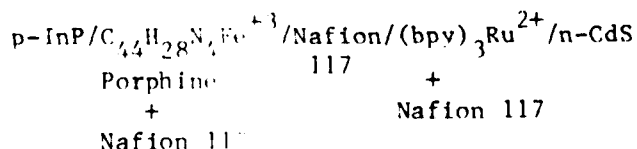
where the respective redox species are initially introduced in a Nafion 117 solution which is subsequently applied onto the surface of a sodium exchange Nafion 117 membrane. The materials and procedures followed for preparation of this cell will now be discussed.

Single crystal n-CdS was obtained from Cleveland Crystal. Ohmic contact to this material was made by initially etching with H_2SO_4 and rinsing with distilled water and drying, followed by contacting with a gallium-indium eutectic. Current collection was achieved to this area via a nickel wire and silver epoxy, and the whole electrode assembly cured at 150°C for one hour.

The p-InP single crystal was obtained from CrystaComm Inc. (Zn doped $\approx 10^{17} \text{ cm}^{-3}$). The $\langle 111 \rangle$ face was used. After etching the surface with a bromine/isopropanol solution, ohmic contact was achieved by the sequential vacuum thermal evaporation of a Au/Zn/Au layer followed by an anneal under H_2 for one hour at 400°C . The cell was prepared by introducing a drop of a 5W/o Nafion 117 present in a mixture of lower aliphatic alcohols containing 0.005M iron (III) meso-tetraphenyl porphine chloride ($\text{C}_{44}\text{H}_{28}\text{ClFeN}_4$) and 0.01M NaCl onto both the surface of an appropriately etched p-InP and a Na^+ exchanged Nafion 117 membrane. After both halves were allowed to nominally dry under ambient conditions for about one hour, they could be directly contacted by lightly pressing. A similar procedure was followed for the photoanode side where a 5W/o Nafion solution containing 0.01M $(\text{bpy})_3\text{RuCl}_2$ and 0.01M NaCl, was introduced onto both the Nafion 117 membrane and n-CdS single crystal before finally being contacted together. A schematic diagram of the finally assembled cell is shown in Figure 1. The simultaneous illumination of both the n-CdS and p-InP redox solid electrolyte junctions was achieved from the n-CdS photoanode side.

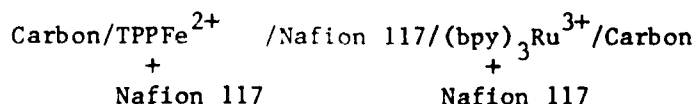
Selection of this two photoelectrode cell was preceded by a preliminary investigation of various redox species introduced into the SPE using cells of the configuration: photoelectrode/redox, Nafion 117/ SnO_2 Cond. Glass. For the cells n-CdS/ $(\text{bpy})_3\text{RuCl}_2$ + Nafion 117/ SnO_2 and p-InP/ TPPFe^{+3} + Nafion 117/ SnO_2 conducting glass, illumination through the conducting glass (100mW/cm^2 quartz-iodine) to the photoelectrode/SPE interface of interest, photopotentials of respectively -750mV and +420mV were realized from each cell. In addition, upon potentiostatting each of these cells respectively 0.4V cathodic or anodic of their illuminated rest potential, current densities in the 3 to $20 \mu\text{A/cm}^2$ range were obtained.

The two photoelectrode cell



approximately one hour after fabrication, possessed a dark open circuit potential of 380mV. Upon illumination of this cell, an initial photopotential of 1130mV was realized. The photoresponse versus time characteristics for this cell are shown in Figure 2. The photocurrent-voltage scan for this cell is shown in Figure 3, both with and without 100mW/cm^2 ELH illumination during cell charge, i.e. the photocathode and photoanode being respectively biased negative and positive of their initial rest potentials. Difficulty has been found to this time in incorporating a meaningful reference electrode in these cells. From Figure 3 the realizable photocurrent was observed to reduce upon increased scan bias. We attribute this to the depletion of electroactive redox species present in the proximity of the respective photoelectrode/SPE junctions. Initial PEC charge currents of $30\text{ }\mu\text{A/cm}^2$ were, however, observed.

The half-cell reactions during cell charge will correspond to $\text{TPPFe}^{3+} + \text{e}^- \rightarrow \text{TPPFe}^{2+}$ at the p-InP photocathode and $(\text{bpy})_3\text{Ru}^{2+} + \text{h}^+ \rightarrow (\text{bpy})_3\text{Ru}^{3+}$ at the n-CdS photoanode. To achieve discharge of these species in the dark, it may be necessary to introduce some appropriate current collection into the proximity of the redox species. To show reversibility for these redox couples the cell



was prepared. The charge/discharge characteristics at $5\text{ }\mu\text{A/cm}^2$ for this cell are summarized in Figure 4. As can be seen, the cycling characteristics were dominated by cell IR losses.

The photocurrent wavelength response of the two photoelectrode cell was performed using a Rudolph Instruments Monochromator Model #681A31. The light source used was a Sylvania 300W ELH bulb. The CdS photoanode was potentiostatted to zero volts relative to the p-InP electrode. The peak photocurrent occurred at $\approx 550\text{nm}$ or 2.25eV (Figure 5), approximately 300mV below the n-CdS band-gap probably due to photoexcitation of the p-InP (band-gap $\approx 1.3\text{eV}$).

In conclusion, we have identified a two photoelectrode solid-state PEC cell which is able to produce photopotentials in excess of one volt and possesses the potential capability for electrochemical energy storage. Such a solid-state cell may eventually find application where a low voltage

photon rechargeable power supply would be required, e.g. to actuate a relay, or for a compact integrating photodetector.

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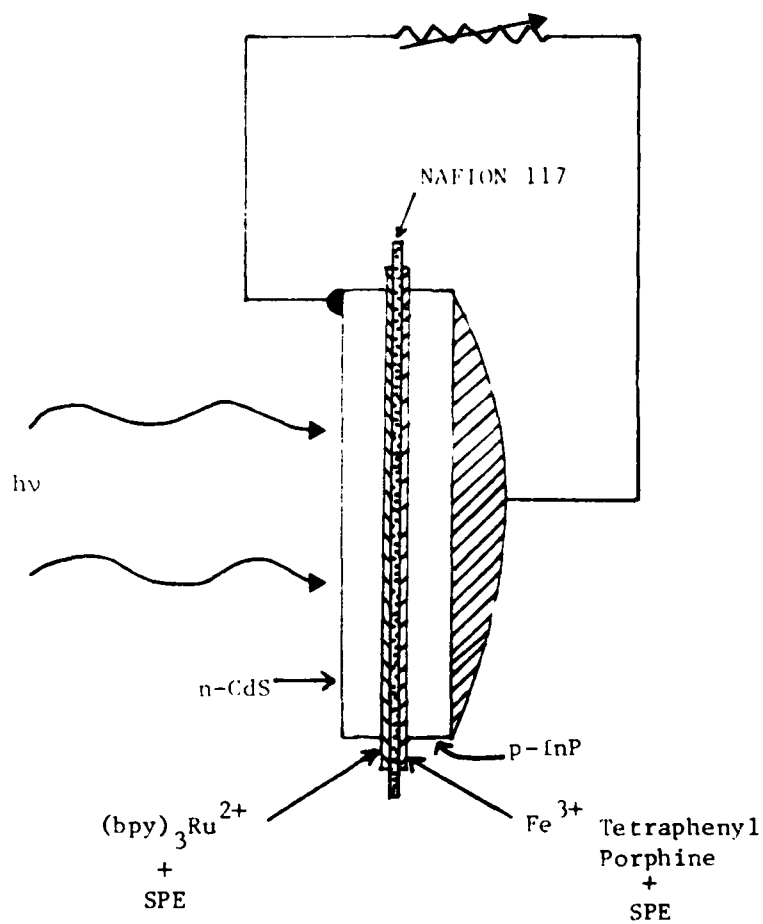


Figure 1.
Schematic Diagram of p-InP/ Fe^{3+} Tetraphenyl Porphine/NAFION 117/ $Ru^{2+}(bpy)_3Cl_2$ /n-CdS
Solid-State Photoelectrochemical Cell.

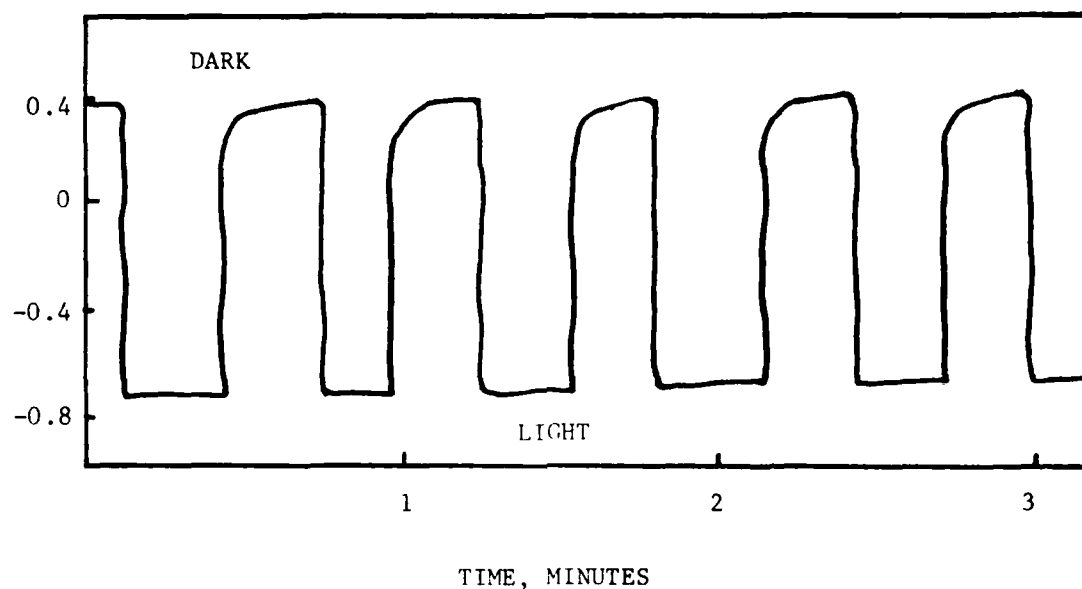


Figure 2. Photoresponse-Time Characteristics for the Cell

Nafion 117	Nafion 117	Nafion 117
p-InP/From Suspension	/Membrane	/From Suspension/n-CdS
+	Na ⁺	+
0.005M C ₄₄ H ₂₈ N ₄ FeCl		0.01M Ru(bpy) ₃
+ 0.01M NaCl		+ 0.01M NaCl ³
Using 100mW/cm ² Quartz-Iodine Illumination		

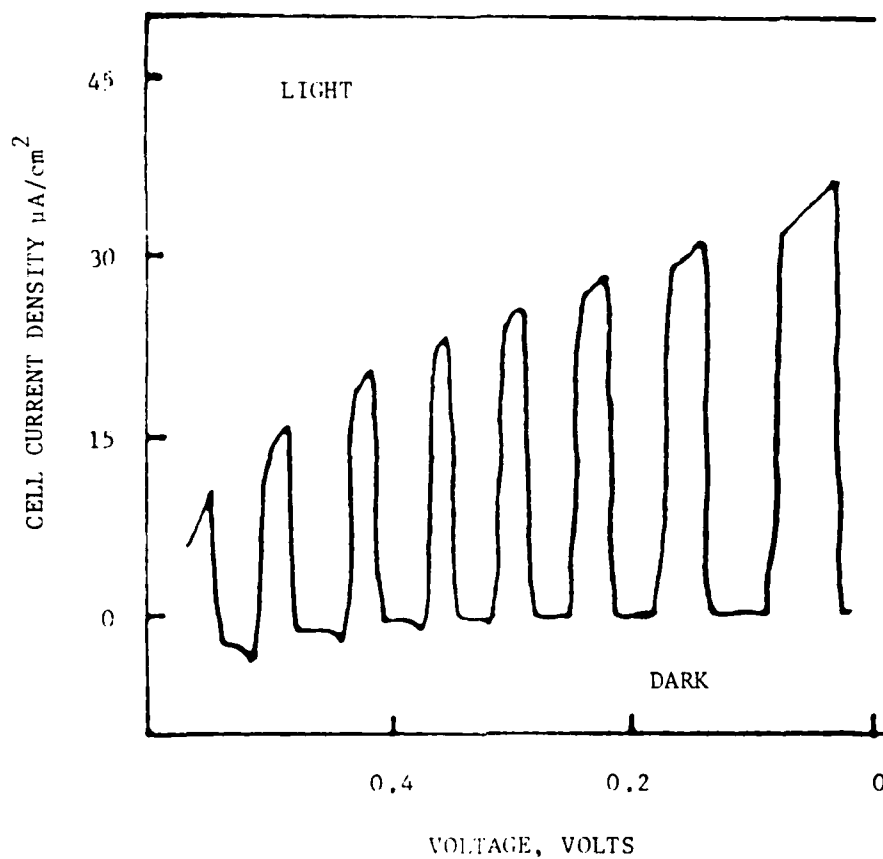


Figure 3. Biased Cell Voltage During Charge for the Cell

p-InP	Nafion 117	Nafion 117	Nafion 117	
/	From Suspension	/ Membrane	/ From Suspension	/ n-CdS
	+ 0.005M $C_{44}H_{28}N_4FeCl$	Na^+	+ 0.01M $Ru(bpy)_3$	
	+ 0.01M NaCl		+ 0.01M NaCl	

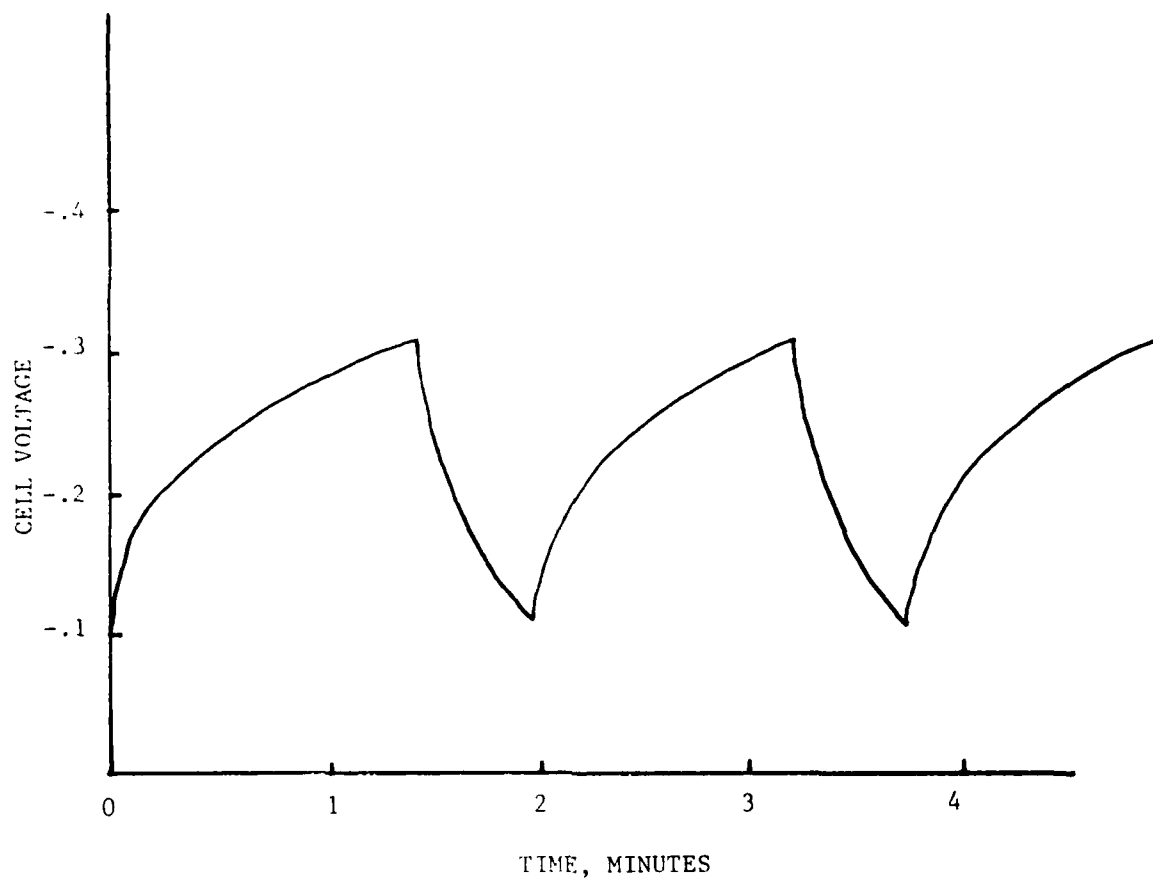


Figure 4. Charge/Discharge Curve for the Cell

Carbon/Tetraphenyl Fe^{+3} Porphine /Nafion 117/(bpy) $_3\text{RuCl}_2$ /Carbon at $5\mu\text{A}/\text{cm}^2$

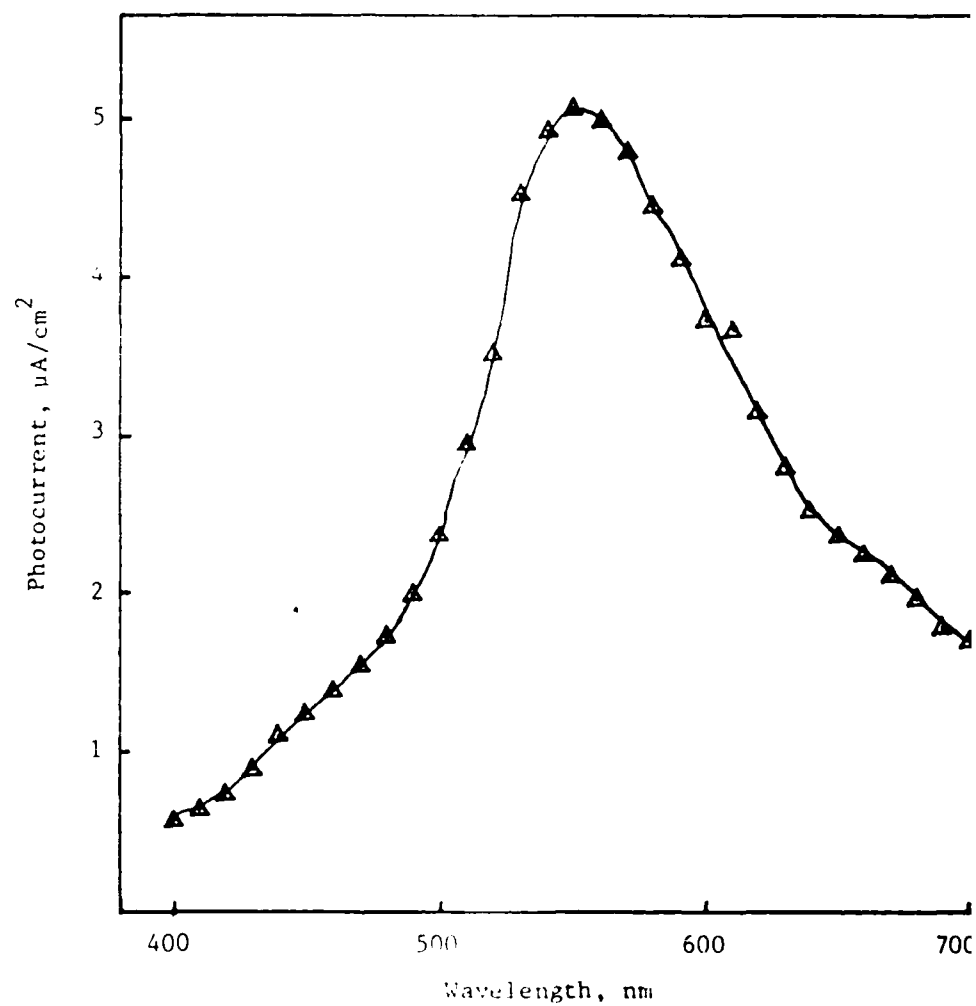


Figure 5. Photocurrent Wavelength Characteristics for the
 $\text{p-InP/C}_{44}\text{H}_{28}\text{N}_4\text{Fe}^{+3}/\text{Nafion}/(\text{bpy})_3\text{Ru}^{2+}/\text{n-CdS}$
 Porphine 117 + Nafion 117
 +
 Nafion 117

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